

***Natural Attenuation of VOCs at Wisconsin Landfills:  
A Preliminary Evaluation***

**Dennis Zuniga  
Bureau of Waste Management – Wisconsin DNR  
September 2002**

## ***Acknowledgements***

The author would like to acknowledge the contributions of Jack Connelly, Environmental Monitoring Team Leader, and Janet Battista, Terry Hegeman, Terry Evanson, and Roger Gerhardt, hydrogeologists with the Wisconsin DNR, for their assistance developing the study concept and design as well as reviewing and editing this document. I also acknowledge the contributions of Loren Brumberg, waste management specialist, and Al Nass, hydrogeologist, with the Wisconsin DNR for their assistance identifying, locating and sampling private wells associated with this study.

## ***Introduction***

This study investigates whether the processes of natural attenuation of volatile organic compounds (VOCs) that function in groundwater at small-scale sites such as spills and leaking underground storage tanks also apply at large-scale municipal solid waste (MSW) landfills. Any one of the following processes can attenuate VOCs: volatilization, sorption, dispersion, dilution, or degradation. At small-scale sites, a natural attenuation process that has been shown effective is that of biodegradation which results in loss of contaminant mass and a reduction in plume size. This investigation evaluated various VOC trends at 31 old, closed landfills throughout Wisconsin in an attempt to answer the following questions:

1. How do VOC concentrations change over time?
2. Does natural attenuation seem to be taking place?
3. What are the principal natural attenuation process/es influencing VOC concentrations at Wisconsin landfills?
4. What role do site characteristics play regarding natural attenuation?
5. What considerations need to be made to assess whether natural attenuation is a valid remedial option?

Based on increased pressure to consider natural attenuation a viable remedial tool and the limited studies of natural attenuation at landfills, we recognized a need to conduct a preliminary assessment of natural attenuation around Wisconsin landfills. In this study, we utilized our extensive database of groundwater monitoring data and built on previous studies of VOCs at Wisconsin Landfills (Battista and Connelly 1989 and 1994; Friedman 1988; Osvath, 1998). These studies established VOCs as the primary substances of concern at municipal solid waste landfills, and that VOCs persist in groundwater many years after landfill closure.

The results of this study will contribute to understanding the natural attenuation processes that occur at MSW landfills throughout Wisconsin where groundwater is contaminated by VOCs. The principles and techniques developed in this study can be refined to be utilized in more-detailed case studies at individual landfills.

## ***Technical Background***

### **Leachate Plume Zonation and Composition**

Landfills are large repositories of undifferentiated organic and inorganic matter. In Wisconsin, if a landfill does not employ advanced engineering controls, these compounds leach to groundwater. Christensen et al. (1994) estimate that organic and nitrogen compounds will leach from landfills for centuries and suggest that most leachate plumes extend to approximately 1000 meters or less from the point of origin.

In the late 1970's, a conceptual model for contaminant zonation downgradient of a landfill was described by Baedecker and Back (1979a). The authors identified a series of distinct redox zones extending

horizontally downgradient from landfills. The redox zones result from microbial degradation of the organic compounds leached from the landfill. Some of the microbial processes require aerobic conditions while others require anaerobic conditions. Moving in the direction of groundwater flow away from the landfill, a release of leachate will allow microbes to easily degrade organic matter by: 1) utilizing dissolved oxygen and nitrate, 2) oxidizing manganese and iron compounds associated with the sediment, 3) reducing sulfate, and 4) producing methane by fermentation and carbon dioxide reduction. If the release of leachate is continuous, these processes lead to steady state conditions and the development of a methanogenic zone close to the landfill where the most degradable organic matter is consumed (Christensen et al, 1994).

Lyngkilde and Christensen (1992a) identified these zones by monitoring the concentrations of oxygen, nitrate, nitrite, ammonium, manganese (II), iron (II), sulfate, sulfide, and methane downgradient from a landfill in Denmark. The zones identified, moving downgradient from the landfill, are methanogenic, sulfidogenic, ferrogenic, manganogenic, nitrate-reducing, and aerobic. The ferrogenic zone was by far the largest and stretched for 350 meters with small and scattered manganogenic zones. At distance, when the oxygen demand in the plume is less than the supply of dissolved oxygen, the plume will again become aerobic. Site specific variations in the distinctiveness of zones, rate of zone formation, and zone size, are related to groundwater velocity and the amount of iron and manganese in the aquifer material (Christensen et al., 1994).

The four main groups of pollutants identified (Christensen et al, 1994) as being present in leachate are as follows:

1. Dissolved organic matter expressed as chemical oxygen demand (COD) or total organic carbon (TOC). This group includes methane, volatile fatty acids, and more refractory compounds that are humic and fulvic. Concentrations of dissolved organic carbon (DOC), can be up to 3,700 mg/l, but rapidly decrease downgradient as the organic compounds are degraded and the leachate is diluted (Baedecker & Back, 1979 b).
2. Anthropogenic organic compounds such as aromatic hydrocarbons, phenols, and chlorinated aliphatics, originating from households or industrial chemicals usually in concentrations less than 1 mg/l.
3. Inorganic macrocomponents: calcium, magnesium, sodium, potassium, ammonium, iron, manganese, chloride, sulfate, and bicarbonate. Since chloride is commonly associated with landfill leachate plumes and is resistant to degradation, it can be used as a conservative tracer for monitoring leachate movement (Christensen et al, 1994).
4. Heavy metals: cadmium, chromium, copper, lead, nickel, and zinc.

Of these classes of pollutants, it is the second group that tends to receive the most attention. The group contains compounds that are of public health and welfare concern even when they occur at concentrations in the low ug/l range. The natural attenuation of some VOCs is slow on the human time scale and may take decades under certain conditions (Wilson et al, 1997). Our study gathered information to assess whether this theory holds up in the field.

In the last ten years substantial research and investigation has been undertaken to develop an understanding of the physical, chemical, and biological processes that affect the migration of VOCs in groundwater. Much of the work has been completed on contamination incidents involving aromatic compounds such as BTEX from petroleum releases and aliphatic chlorinated solvents. Those types of sites are easy to characterize and cleanup because of the finite source and ability to remove the bulk of the source material. However, landfills differ in that they are nearly infinite sources of contamination and source removal is, in most cases, financially restrictive. Additionally, landfills represent a more complex situation since pollutants from all four classes identified above may be present.

## Background Summary

Battista and Connelly (1994) examined VOC concentrations at 11 closed landfills in Wisconsin that had been previously studied in the late 1980s and found that VOC concentrations had declined initially but did not show continued decline over time. This raised questions as to whether the reductions in concentration were due to dilution, source reduction, or degradation and whether conditions have changed at the sites. As mentioned earlier, the Wisconsin Department of Natural Resource (WDNR) is receiving increased pressure to accept natural attenuation as an acceptable remediation technology for contaminant problems at landfills.

Natural attenuation processes may reduce the potential risk posed by VOC contaminants in groundwater in three ways: (1) Transformation of contaminant(s) to a less toxic form through destructive processes such as biodegradation or abiotic transformations; (2) Reduction of contaminant concentrations, by processes such as dilution and dispersion, whereby potential exposure levels may be reduced; and (3) Reduction of contaminant mobility and bioavailability through sorption onto the soil or rock matrix.

It also should be noted that some natural attenuation processes might result in the creation of transformation products that are more toxic and/or mobile than the parent contaminant (e.g., degradation of PCE and TCE to vinyl chloride). The potential for creation of toxic transformation products is greater at non-petroleum release sites (e.g., chlorinated solvents or other volatile organic spill sites). Although some studies have shown that vinyl chloride can be degraded under certain conditions (McCarty, 1997), each site should be evaluated to determine if implementation of biodegradation is appropriate and protective in the long term.

## ***Procedures***

To assess the natural attenuation processes occurring at MSW landfills throughout Wisconsin we: selected landfills based on data requirements, chose VOC compounds to include, collected site characteristics, performed trend analyses, and conducted sampling at private water supply wells within 1200 feet of closed landfills.

### **Landfill Selection**

We selected 31 closed municipal solid waste landfills throughout Wisconsin to determine trends of VOC concentrations in groundwater through time. The selection of the 31 landfills was based solely on the information contained in WDNR's database, the Groundwater and Environmental Monitoring System (GEMS), and the Bureau of Waste Management's files. Every landfill that is required to collect environmental monitoring data is included in the GEMS database. First, we selected only landfills with active groundwater monitoring that are closed or in the process of closing. That selection criterion narrowed the field of 622 total licensed landfills down to 384. Of the 384; 267 landfills accepted primarily MSW. That number was reduced to 114 by selecting only landfills that monitored groundwater for VOCs at any time in their history. These 114 remaining landfills were reduced to 50 by requiring that at least one monitoring point have a 10-year record of VOC data. From 50 the field was narrowed to 34 by ranking the remaining landfills based on the number of times the 22 most common VOCs were detected in samples. Three of the 34 landfills were eliminated in the process of site characterization or trend analysis based on insufficient data. We evaluated the remaining 31 landfills with the most complete site characterizations and VOC data.

### **Contaminants of Concern Selection**

In order to limit the amount of data analyzed we consolidated the list of individual VOCs into groups. We wanted to include the most commonly detected compounds related to MSW landfills and the compounds that are associated with their degradation and/or generation. We consolidated the list of 49 Volatile Organic Compounds contained in section NR 507, Appendix 3, Wisconsin Administrative Code, into two main groups, BTEX and Chlorinated Aliphatics. The BTEX group contains Benzene, Toluene, Ethylbenzene, and total Xylenes. Included in the Chlorinated Aliphatics are Tetrachloroethene (PCE), Trichloroethene (TCE), cis 1,2-Dichloroethene (cis 1,2 DCE), trans-1, 2-Dichloroethene (Trans 1,2 DCE), Vinyl Chloride, 1,1,1-Trichloroethane (1,1,1 TCA), 1,1,2- Trichloroethane (1,1,2 TCA), 1,1-Dichloroethene (1,1 DCE), 1,1-Dichloroethane (1,1 DCA), 1,2-Dichloroethane (1,2 DCA), and Chloroethane. In addition, we looked at the original 49 compounds as a whole to determine the relationship between the complete list, the BTEX group, and the Chlorinated Aliphatics. The purpose of segregating the list of the 49 compounds into these three groups was to limit the complexity of looking at trends for 49 compounds at 31 landfills and making comparisons between individual compounds.

### **Trend Analysis**

#### ***Trend Construction***

We summed the VOC concentrations from all the wells at a particular landfill sampled on a given date and compared those summations through time. This technique depicted the trend through time of the total mass of VOCs in the groundwater in a region around the landfill defined by the wells included in the summation. To keep the region defined through time stable, we limited the wells used at each landfill. We included only the wells that were sampled on the same dates throughout the monitoring history of the landfill. This was done to normalize the data and to limit the effect that including or excluding wells

throughout the landfill's monitoring history might have on the summation of concentrations. For example, if we started looking at the total VOC concentration that three wells contributed early on and later we looked at the total VOC concentration contributed by six wells, we might see a false increasing trend. To include as many wells for a particular landfill as we could we created multiple groups of wells that were sampled on similar dates and constructed trends for each of these groups. The grouping of wells was primarily based on the frequency of sampling. Often the frequency of sampling was determined by review staff based on locational factors so in some cases the groups were also related spatially. Consequently, each landfill may have two or more regions, defined by groups of wells, for which we have developed trends. Overall trends for each landfill were determined by a weighted evaluation of the individual trends for all the well groups at a landfill. In most cases, each group of wells at a landfill showed the same type of trend. Where there were discrepancies between groups, the trend from the group of wells that best characterized the landfill was determined to be the overall trend. We followed the same methodology for constructing trends of total BTEX and total Chlorinated Aliphatics. All three trends, for a specific group of wells, include the same wells and the same sample dates in order to make comparisons between them.

### ***Statistical Application***

We applied a Mann-Kendall statistical test, using a 95% confidence level, to all the trends for the three groups of VOCs and each group of wells at all landfills. We performed this test to verify that the trends we see graphically are also statistically valid. There are four possible outcomes with the Mann-Kendall test: Increasing, Decreasing, Stable, or Undetermined trend. An increasing outcome signifies that the concentrations of a particular contaminant, or groups of contaminants, are increasing through time, while a decreasing outcome means that the concentrations of a particular contaminant, or groups of contaminants, are decreasing through time. A stable outcome occurs when there isn't enough variation in either direction to determine an increasing or decreasing trend. Finally, an undetermined trend occurs when there is so much variation that no trend can be determined, statistically.

### ***Inorganic Parameter Selection and Trend Construction***

To determine the processes that affect the concentrations of VOCs at each landfill, we looked at inorganic parameter trends at each landfill. The chosen parameters are known to either biologically mediate the breakdown of certain VOCs or indicate those processes are occurring. Specifically, the inorganic parameters we looked at were chemical oxygen demand (COD), alkalinity, hardness, chloride, iron, and in some cases sulfate and manganese. We constructed time vs. concentration graphs that compare total VOCs to each one of the inorganic parameters listed above. We also performed the same Mann-Kendall statistical test as we did with the VOC trends to compare the two using a common statistical reference. Comparing the inorganic trends to the total VOCs trends was done to add supporting evidence where degradation was thought to be occurring.

### ***Summation Validation***

We looked at total VOC trends of each individual well and compared those trends to the trends of the summation of all wells. This was done to determine the effect the summation of concentrations had on the overall BTEX, Chlorinated Aliphatics, and total VOC trends we observed.

## **Site Characteristics Data Collection**

The information regarding the site characteristics and remedial actions was obtained almost entirely from the Bureau of Waste Management (BWM) files. The main categories of data we attempted to collect were site hydrogeology, gross site geology, waste types and volumes accepted, location of monitoring wells in relation to waste mass, and remedial actions taken. The types of information we were able to obtain for all of the landfills were groundwater flow direction, general site geology, waste volumes, and the layout of the monitoring well network. The layout of the monitoring well network was obtained from the most

recent facility plan sheet and the wells were matched to the analytical data with the information contained in the BWM's groundwater and environmental monitoring system (GEMS) database. General site geology was determined based on GIS data layers developed by the Wisconsin DNR and Wisconsin Geologic and Natural History Survey (WGNHS). The landfill characteristics were entered into a database to facilitate data summary and table creation.

### **Private Well Selection**

Well drillers are required to obtain a variance from the DNR prior to installing a private well within 1200 feet of a landfill. Included in this study is an evaluation of select private wells that are located within 1200 feet of a landfill. Our initial intent for including private well sampling in this study was to look at only those wells that had been granted variances but, due to time constraints and the difficulty in identifying wells that have been granted variances, this restriction was relaxed. Wherever possible we sampled wells known to have been granted a variance for construction within 1200 feet of a landfill. The majority of wells were selected by a solicitation to DNR staff asking whether they knew of any private wells that were near landfills where VOCs were a concern.

## ***Findings***

### **VOC Trend Analysis**

Approximately 21 groundwater monitoring wells were included in the trend analyses for each landfill based on an average of two groups per landfill. A summary table (Table 1) displays the overall trends for each of the landfills.

During the trend analysis, it became evident that the chlorinated aliphatics contributed a greater percentage of the total VOC concentrations than the BTEX compounds. In fact, the majority of BTEX trends were at such low levels that the resulting plots were episodic with many peaks and valleys of varying concentrations, which led to a disproportionate number of undetermined BTEX trends. Twenty-one of 31 landfills had total BTEX levels stabilized below 20 µg/L while the same number of landfills had total chlorinated aliphatics levels stabilized below 100 µg/L. The low concentrations and extreme variability made it difficult to correlate BTEX trends to the other two groups of compounds.

We compared the number of landfills that showed the same overall total VOC and chlorinated aliphatics trends and saw that 23 of the 31 landfills agreed. All of the landfills that had a decreasing trend with respect to total VOCs also had decreasing trends with respect to chlorinated aliphatics. Further, of the 10 landfills that had a stable total VOC trend, seven also had a stable chlorinated aliphatics trend. By contrast, only four out of 10 landfills had a stable BTEX and total VOC trend. It should be noted that two out of the 10 landfills had an undetermined BTEX trend and there was only one undetermined trend for the chlorinated aliphatics. Additionally, all landfills with stable total VOC trends had stable or decreasing chlorinated aliphatics and BTEX trends, with the exception of the two undetermined BTEX trends and the one undetermined chlorinated aliphatics trend previously mentioned. It was not meaningful to compare increasing or undetermined trends since there were only three landfills that had an increasing total VOC trend and undetermined trends cannot be correlated.

Interestingly, we found a higher number of landfills showing a decreasing trend for the chlorinated aliphatics (15 of 31) than the BTEX (10 of 31) compounds. However, we had to consider that 14 of 31 landfills had undetermined trends for BTEX while only five of 31 landfills had undetermined trends for the chlorinated aliphatics. In other words, 10 of the 17 trends that were determined for the BTEX group and 15 of the 26 trends that were determined for the chlorinated aliphatics showed a decreasing trend.

### **Inorganic vs. VOC Trend Analysis**

The inorganic data that we considered for each landfill were used primarily as supporting evidence, where possible, for what was observed in the VOC data. However, we did find one interesting relationship between the inorganic species and the VOCs at a number of landfills.

While plotting the inorganic trends, it appeared that a large number of the inorganic trends seemed to track the various VOC trends. An example of what is meant by tracking is illustrated in Figure 1. As is shown in Figure 1, both the inorganic and VOC trends vary in the same manner between sampling events. We would expect this for nitrate and sulfate (electron acceptors) but not for iron, chloride, manganese, hardness, or alkalinity if degradation, either chemical or biological, were taking place. This seemed to suggest that the physical processes of natural attenuation such as dilution and dispersion played a major role in the levels of both the VOCs and the inorganic parameters site-wide.

To determine how many inorganic trends actually tracked total VOC trends, we counted the total number of inorganic trends that we produced and established the number of those that visually tracked the total VOC trends. Initially, we tried to run a statistical correlation test to evaluate which inorganic trends



tracked the total VOCs trends but the statistical test was prohibitively time consuming and seemed to ignore the similar variations on short time scales. Consequently, we chose to visually correlate the two types of trends, which is much less systematic but also allows for some informed judgment. About 35% (111 of 317) of the inorganic trends closely tracked the total VOC trends. The total number of trends determined for nitrate and sulfate, the two species expected to track total VOCs if degradation is taking place, was 19 total (3 nitrate and 16 sulfate). Surprisingly, about 1/3 of the inorganic trends that are not expected to track total VOCs (iron, chloride, manganese, hardness, and alkalinity) actually do. For comparison, the number of inorganic trends that showed an opposite trend to that of the corresponding total VOC trend was 27 of 317 or 9%.

## Site Characteristics

The reliability of the site characteristic data collected was not consistent because of the variation in the sources and completeness of the files for each individual landfill. A basic summary of the information we gathered on each landfill follows.

The hydrogeologic data that we collected on each landfill were very inconsistent from landfill to landfill so it was difficult to say whether a landfill with certain hydrogeologic conditions was more suited for natural attenuation than others. The only consistently reliable hydrogeologic data that we obtained was groundwater flow direction. The groundwater flow directions were considered reliable given that it has been the policy to monitor and report groundwater elevations on a regular basis for some time. Within the scale that we were interested in, groundwater flow directions do not often change dramatically within a ten-year period. Generally, it is assumed that contaminants, including VOCs, travel in the direction of groundwater flow. During the course of this study, we did not see any evidence to the contrary, so we believe this assumption holds true. From this, it seems more useful to consider hydrogeology on a landfill by landfill basis rather than trying to generalize between landfills with similar hydrogeologic conditions.

The geologic information supplied by the reports in the files was too inconsistent to compare between landfills. Consequently, we used WGNHS regional geologic maps to identify the surficial deposit type, bedrock type, and approximate depth to bedrock for each landfill. Commonly, significant geologic variation can occur at an individual landfill, so caution must be taken when considering these data because of their regional scale. The three geologic categories for each landfill are included in Table 1. It is interesting that the three landfills that show an increasing total VOC trend are all in a sandstone bedrock environment each with different surficial deposits. The same proportions of the three bedrock environments are present for each of the three remaining total VOCs trends. The surficial deposits show the same lack of correlation between deposit type and total VOC trend type. These data do not suggest that any one type of geologic material is intrinsically better at controlling VOC contamination at landfills in Wisconsin.

We obtained waste volume estimates in cubic yards for all 31 landfills we looked at. We grouped each of the 31 landfills into one of three categories based on estimated size of fill. Large landfills were those with estimated capacities of 500,000 cubic yards or more, medium landfills were those with 50,000-500,000 cubic yards, and small landfills were those with less than 50,000 cubic yards. There were 13 landfills classified as large, 18 landfills as medium, and no landfills fell into the small category. Next, we determined how many landfills in each of the two categories had increasing, decreasing, or stable trends for the three groups of VOCs.

The large size classification contained 2 of the 3 landfills that had increasing total VOC trends. This may indicate that the larger landfills are contributing more VOC contaminated leachate to groundwater and that the natural attenuation processes are not acting sufficiently to limit the VOC levels in groundwater.

More significantly, the most frequent trend observed at the large landfills (5 of 13) was a decreasing trend for total VOCs while at the medium landfills a stable trend was most frequent (7 of 18). Undetermined trends were equally represented by both large and medium landfills. The ratios discussed above roughly hold true for the chlorinated aliphatics group as well, but the BTEX group has a disproportionate number of undetermined trends the reasons for which were discussed in the trend analysis section of the findings.

## **Remedies**

We looked at the remedial actions that were taken at each landfill. The information we gathered about each landfill in regards to remedies was incomplete. In most cases, we know what types of remediation were employed at each landfill but the timing is approximate. Consequently, the following is a summary of landfills we knew had remedies installed and the various trends those sites exhibited.

We identified 13 landfills that had an active gas extraction system installed. (Table 2) When we considered total VOC trends we found that two of the 13 landfills with active gas extraction systems were increasing, three were decreasing, four were stable, and four were undetermined. For the chlorinated aliphatics trends, there was only one landfill that was increasing, five decreasing, five stable, and two undetermined. The BTEX trends show the same type of scattered counts. The data suggest that gas extraction may be effective in stabilizing chlorinated VOC contaminant plumes and the effectiveness of any particular gas extraction system in controlling VOC levels in groundwater is dependent on site specific conditions.

We identified seven landfills with a clay liner and three landfills with leachate extraction. Although clay liners are not generally considered remedies, our discussion of clay liners is included here because the presence or absence of a liner impacts the performance of other remedies. Most notably in regards to the clay-lined landfills, four of seven exhibited decreasing chlorinated aliphatic trends. All three landfills that had leachate extraction showed decreasing total VOC and chlorinated aliphatics trends and two out of the three had decreasing BTEX trends with the third landfill having an undetermined BTEX trend. (Table 2)

We identified two landfills with a groundwater extraction system in place, Winnebago County and the City of Shawano landfills. Both landfills showed a decreasing trend for the chlorinated aliphatics and an undetermined trend for BTEX. The total VOC, chlorinated aliphatics, and BTEX trends for the City of Shawano landfill showed a rapid decrease after 1986 when the groundwater extraction system was constructed and concentrations of each contaminant group have stabilized or declined since. In contrast, the Winnebago County landfill showed a marked decline in concentrations only for the chlorinated aliphatics group of compounds following construction of the groundwater extraction system.

## **Validation of Well Summation Procedure**

Summing the concentrations for all the wells at a landfill was done to obtain an overall picture of the mass of VOC contamination at each landfill. The clarity of the overall picture depended on how well the landfill was characterized by the monitoring well network. For the purposes of this study, we assumed that each landfill was adequately characterized by the wells included in the trend analysis. On average, there were 22 wells per landfill. Wherever possible we considered any additional information we gathered from the landfill files to verify that assumption. As mentioned in the procedures, we tested the effect that summation of well concentrations had on the total VOC trends by comparing the trends for total VOCs in individual wells and total VOCs in all wells.

Twenty-two of the 31 landfills showed good visual correlation between the total VOC trends in all wells to the total VOC trends for the individual wells. Figure 2 is an example of what was considered good

visual correlation. This suggests the processes affecting the trends observed are working on a site-wide basis.

### **Private Well Sampling**

We took samples from 21 private wells located within 1200 feet of six different closed landfills. One of the landfills was included in this study (WMWI-Reclamation), one was a landfill that was suggested by a staff member, and the remaining four were sites on the registry of waste disposal sites. Four wells were sampled in southeastern Wisconsin, five wells were sampled in northeastern Wisconsin, and 12 wells were sampled in west central Wisconsin. There were no detects in any of the wells sampled in southeast or northeast Wisconsin and six compounds detected at four wells in west central Wisconsin. All detects were below groundwater quality standards and only one result was above the lab-calculated limit of quantitation. The compounds that were detected were N-Hexane, Methylene Chloride, Trichlorotrifluoroethane, Tetrahydrofuran, and M/P-Xylene. Of those five compounds, Methylene Chloride and Tetrahydrofuran are known lab or monitoring well construction contaminants. Only one of the landfills (WMWI-Reclamation) near the sampled private wells was known to have significant VOC contamination and the associated private wells had no contaminants detected in the water samples. Although the sample population was small and the majority of the landfills have no significant groundwater contamination, the fact that isolated VOCs were detected demonstrates the need to further investigate the adequacy of WDNR's variance procedures for private wells located within 1200 feet of landfills.

## Discussion

### Observations:

- The development of VOC concentrations in groundwater at MSW landfills follows a general progression of rapid decline, followed by a period of much slower decline, and finally a stabilization phase where concentrations approach an asymptotal level.
- The majority of closed MSW landfills included in this study exhibited a stable or decreasing trend with respect to total VOC concentrations.
- Total BTEX concentrations are generally much less than total chlorinated aliphatics.
- Cis 1,2 DCE appears to be the primary contributor to the total chlorinated aliphatics concentrations at the majority of the landfills and its presence suggests that reductive dehalogenation is taking place.
- The highest concentrations of the BTEX compounds were present at the water table wells near the waste mass while the highest concentrations of chlorinated aliphatics were found in the deeper piezometers downgradient from the waste mass.
- A large number of inorganic trends closely match those of the total VOCs.
- Gas extraction may decrease or stabilize the concentrations of chlorinated VOCs based upon data from the limited number sites evaluated in this study.

### *How do VOC concentrations change over time?*

Rice and others (1995) formulated a conceptual model of hydrocarbon plume development that Mace, et al. (1997) used as a basis for their study of leaking petroleum storage tanks in Texas. This model described four phases of plume mass development: an initial increase (phase 1), stabilization (phase 2), exponential decrease (phase 3), then slow decrease to zero (phase 4). Monitoring for VOCs at Wisconsin landfills has only quite recently become routinely required so the data we collected in this study only captures the last two or, possibly, three phases of plume development. Landfills represent much larger sources of contaminants than do leaking petroleum storage tanks, which results in an increased temporal residence in each of the phases. Because of the increased resident time of the phases, it is possible to identify sub-phases of plume development. Phase 3 is where the majority of the landfills in this study start out their monitoring history and remains as a single phase. Phase 4 can be broken down into two sub-phases where the first is a slowing down of the decline in concentration and the second is a stabilization to an asymptotal concentration, usually greater than zero. The natural progression between phases can be disrupted by remedial events whereby a phase can be restarted or bypassed.

### *Does natural attenuation seem to be taking place?*

If we see a reduction in concentrations over time, we can say definitively that natural attenuation is taking place only if no man-made remediation has occurred. In an effort to protect public health, the landfills that are included in this study, VOC contaminated landfills all have had one remedy or other employed so a reduction in contaminant concentrations alone may not accurately assess whether or not natural attenuation is occurring. However, during our assessment of the various remedies employed at MSW landfills we saw no significant correlation between remedy type and concentration trends. Therefore, any trends that have been either decreasing or stable for seven to ten years indicate that some or all the processes of natural attenuation are occurring. There were 20 of 31 (65%) landfills that exhibited a stable or decreasing total VOC trend and we were unable to determine total VOC trends for 8 of 31 landfills. Furthermore, it is assumed that any contaminant leached into groundwater will be subject to the physical processes of natural attenuation such as dispersion and dilution. Based on our findings it is evident that natural attenuation does occur at the majority of MSW landfills in this study and probably at the majority of all others. However, it must be pointed out that natural attenuation can occur via both destructive and nondestructive processes. For example, a plume can be decreasing in concentration but expanding spatially due to dilution and dispersion effects. The plume is being naturally attenuated but the risk to

additional receptors may be increased. Although natural attenuation is occurring, we did not gather evidence to determine whether to expect contaminated wells to reach levels below groundwater standards.

*What are the principal natural attenuation process/es influencing VOC concentrations at Wisconsin landfills?*

Natural attenuation can occur via physical, chemical, or biological processes and the cumulative result is a reduction in contaminant concentration. Three processes seem to be the principle actors influencing natural attenuation of VOCs at Wisconsin landfills. Dilution is the most influential abiotic process that affects all three groups of VOCs. The high number of inorganic trends that matched the trends for total VOCs indicates that dilution (infiltration) is controlling both the various inorganic and VOC concentrations at about 1/3 of the landfills studied. Chemical or biological processes cannot explain the amount of similarity in the trends between chemically dissimilar species. Another line of evidence supporting dilution as the principal abiotic process is the significant amount of correlation between trends for the summation of concentrations at all wells and the trends for individual wells at a landfill. The other two principal, natural attenuation processes are aerobic and anaerobic degradation. Aerobic degradation is most important when considering the BTEX compounds, cis 1,2 DCE, and vinyl chloride. The BTEX compounds were most often detected in wells screened at the water table or shallow piezometers and thus were subject to more oxygen-rich groundwater. The episodic nature of the BTEX trends observed might have been the result of the infiltration of oxygenated water by precipitation events. Previous literature indicates that cis 1,2 DCE and vinyl chloride degrade most rapidly under aerobic conditions. However, these compounds are primarily the result of the reductive dechlorination of TCE and PCE so their presence indicates an anaerobic environment. The result at a large number of landfills is a reduction of TCE and PCE and rapidly increasing concentrations of cis 1,2 DCE with minor concentrations of vinyl chloride. The final process by which natural attenuation is occurring is anaerobic degradation. Wiedemeier, et al suggest that highly chlorinated solvents such as PCE and TCE degrade most readily in anaerobic conditions via reductive dechlorination. It was assumed that the BTEX compounds represented a significant oxygen sink because concentrations were much lower relative to the chlorinated aliphatics at the majority of the landfills. However, BTEX compounds remained present at the bulk of the landfills, which led us to believe that anaerobic conditions were prevalent. Cis 1,2 DCE is primarily a degradation by-product and the high levels we observed indicate that anaerobic degradation of PCE and TCE had occurred at most landfills.

*To further illustrate the degradation processes relating to the chlorinated ethenes a more detailed discussion of a few landfills follows.*

***Chlorinated ethenes degradation pathways***

We looked at the chlorinated aliphatics group and the PCE - TCE - (cis/trans) DCE - Vinyl Chloride degradation pathway at a few landfills. We chose this particular degradation pathway because the majority of the contaminant mass at the landfills was from the chlorinated aliphatics group and the chlorinated ethene degradation pathway is relatively straightforward and well studied. We compared the contribution of each chlorinated ethene compound to the total of all chlorinated ethenes through time in an attempt to determine if degradation was taking place. We created charts for at least one landfill in each of the three trend categories (increasing, decreasing, or stable) to see what each type of trend exhibited with respect to degradation.

***Increasing Example***

A landfill with an increasing VOC trend we chose to study was Metropolitan Refuse District Landfill. There are glacial deposits overlaying sandstone bedrock at this landfill. The depths to bedrock range from 20 feet in the southwest part of the landfill to about 70 feet in the north. This landfill consists of two fill areas; one accepted about 600,000 cubic yards of MSW from 1961 until 1981 and the other accepted

about 400,000 cubic yards of MSW between 1981 and 1996. Both fill areas were capped with a composite cover, the older in 1992 and the newer in 1994. At the time the new fill area was capped an active gas extraction system was installed. We chose this landfill because it had fairly high levels of VOCs and in spite of a composite cap, gas venting, and more recently gas extraction, the concentrations of VOCs in groundwater were increasing. At this landfill cis 1,2 DCE contributed about 80% of the combined total concentration, and PCE, TCE, cis 1,2 DCE, and Vinyl Chloride concentrations stayed relatively stable. (Figure 3) Trans 1,2 DCE was at such low levels that it was insignificant compared to the other four compounds. These data suggest that degradation is taking place but stagnates once it reaches cis 1,2 DCE or that there is significant levels of cis 1,2 DCE in the leachate from this landfill. As a rule of thumb, if the ratio of cis 1,2 DCE to Trans 1,2 DCE plus 1,1 DCE is greater than about 5:1, the DCE is probably of biogenic origin. (Wiedemeier, et al.) Since the ratio in this case is greater than 5:1 and it is assumed that landfill leachate is not a significant source of cis 1,2 DCE, it is almost certainly the case that degradation is the cause for the high levels of cis 1,2 DCE. An additional observation that was made is that the transformation between species is apparently happening at a steady pace. This is evident if we look at the same trend on a percentage basis. (Figure 3)

### ***Decreasing Example***

For the case of decreasing VOC levels, we chose to study the Rice Lake landfill (Figure 4) because there was a strong decreasing trend and only one group of wells to look at. This landfill was constructed in glacial sediment overlying Cambrian sandstone and/or Precambrian Quartzite. Approximately 400,000 cubic yards of municipal solid waste was disposed of between 1964 and 1983 and 471,000 cubic yards of demolition waste was landfilled between 1983 and 1990. The landfill was closed and capped in 1990 with a cap upgrade in 1996. In regards to the parent species, PCE and to a lesser extent TCE, we saw a steady to slightly decreasing trend with respect to concentrations. The wells at this landfill are in close proximity to the landfill so we can assume that the steady levels of PCE and TCE correspond to a steady source of chlorinated ethenes to groundwater. We then looked at the daughter products and saw that initially there were high levels of both cis 1,2 DCE and Vinyl Chloride. The Vinyl Chloride has persisted throughout while the cis 1,2 DCE has declined to near zero by the end of our monitoring history. This suggests that the parent species, PCE and TCE, are readily degrading to cis 1,2 DCE which in turn is degrading rapidly to Vinyl Chloride. In addition, the Vinyl Chloride levels are decreasing which indicates that significant degradation of Vinyl Chloride is taking place. It is also interesting to note the timing of the installation of the GCL cap in 1996 and its affect on the trend. The trend seems to restart after the cap was installed, which supports the idea that VOC plumes reach equilibrium at some point in their history.

### ***Stable Example***

An example of a landfill that had stable VOC trends was the City of Waupun landfill. The geology at this landfill consists of loess underlain by glacial till which, in turn, is underlain by Platteville-Galena dolomite. The depths to the fractured dolomite bedrock range from 5-22 feet below the surface. The city of Waupun accepted both MSW and demolition waste during operations between 1975 and 1991 and the total waste that was landfilled was estimated at 200,000 cubic yards. What we saw when we graphed out the chlorinated ethenes was that the parent species were present initially and decreased in concentrations steadily until PCE was near zero and TCE was about 1/5 of its original concentration. (Figure 5) During the same time that the parent species were declining the daughter product, cis 1,2 DCE, was increasing. Throughout the monitoring history, trans 1,2 DCE and vinyl chloride were at fairly steady concentrations. Here it seems that an increasing cis 1,2 DCE concentration made up for the decline in PCE and TCE concentrations that led to an overall stable chlorinated ethene trend. This points out the utility in considering the ethene concentrations as a group as well as individually.

### ***Other Significant Cases***

An interesting landfill was the City of Durand Landfill. (Figure 6) This landfill is located in glacial sand & gravel outwash deposits underlain by Cambrian sandstone probably of the Eau Claire Formation. The landfill accepted municipal solid waste from 1968 until 1990 with a final capacity of about 240,000 cubic yards of waste. The landfill was closed and capped in 1991 with a geosynthetic composite cap. The wells at this site can be placed into three groups based on distance from the landfill. Only two of the groups had significant data because one of the groups of wells had only three water table wells located quite a distance from the fill. The first group of wells consisted of four water table wells and one piezometer all located within 100 feet of the waste mass. When we looked at the chlorinated ethenes and their relative concentrations at the group 1 wells we saw high levels of cis 1,2 DCE and Vinyl Chloride, initially, then the levels decreased steadily throughout the monitoring history with minor concentrations of PCE that showed the same trend.

The group 2 wells, further downgradient and primarily piezometers, showed a remarkably different trend. These wells began with somewhat low levels of cis 1,2 DCE and even lower levels of Vinyl Chloride only. Towards the middle of the monitoring history, we began to see PCE and then TCE that started at low levels and steadily increased. Meanwhile the levels of cis 1,2 DCE and Vinyl Chloride were also steadily increasing. It is interesting to note that the group 2 wells are all over 1000 feet from the waste mass. It appears from the group 1 wells near the fill that significant degradation is taking place to limit the chlorinated ethene levels in groundwater. However, the fact that we see first the presumed products of degradation and then the parent species quite a distance from the landfill introduces some doubt about how effective degradation is at limiting contaminant migration. The idea that the plume is sinking below the water table wells in group 1 and migrating downgradient towards the deeper piezometers in group 2 seems to be a viable explanation. This is supported by the fact that we see higher levels of PCE in the distant group 2 wells than we see in the much closer group 1 wells. (Figure 6) If we assume that PCE is primarily a source product then this is the most reasonable explanation.

Another interesting site was the City of Boscobel landfill, which is located in a pre-glacial bedrock valley filled with glacial sand and gravel deposits overlying bedrock consisting of Prairie du Chien dolomite and Cambrian sandstone. The depth to the dolomite bedrock ranges from 14 -77 feet and dips north. The landfill accepted MSW from the late 1950s until 1982 and accepted hazardous waste from 1968 to 1977. The landfill was capped initially in 1985 with final closure and a cap upgrade in 1992. The total VOC and chlorinated aliphatics concentrations show a steady decreasing trend for the full 14 years for which there is data. There were six wells included in the trends we constructed for this landfill and all were within 100 feet of the waste mass. When we looked at the relative proportions of the individual chlorinated ethenes we noticed that 80-100% of the total ethene concentration was contributed by PCE. (Figure 7) Since PCE is decreasing and the daughter products aren't showing up in increasing concentrations, it seemed that the source of the contaminants must have been producing the trend we saw. The only source controls used at this landfill were the two capping events. The waste was first capped in 1985 prior to any VOC data that we have so we cannot verify the cap's influence on the decline we saw. However, the cap upgrade in 1992 does not seem to affect the trend at all, leading us to believe that the cap may not be the best explanation for the decline. This landfill was also unusual in that there were higher levels of 1,1,1 TCA and 1,1 DCA than any of the ethenes. When we compared the relative contributions of 1,1,1 TCA and 1,1 DCA, we saw a relationship more indicative of degradation. (Figure 8) The concentrations of 1,1,1 TCA decreased while the concentrations of 1,1 DCA were stable. We saw that on a percentage basis 1,1,1 TCA decreased while 1,1 DCA increased in relation to the total. Alkalinity levels increased while the total VOCs and chlorinated aliphatics concentrations decreased which taken together is an indication that biodegradation is occurring. This landfill illustrates the complexities that are inherent at each individual site adding to the difficulty in generalizing between sites.

### *What role do site characteristics play regarding natural attenuation?*

The geology and hydrogeology of an individual landfill is most important in relation to the physical processes of natural attenuation. We have identified the most significant physical, natural attenuation process as being dilution. The geology and hydrogeology of a site impacts dilution by controlling the amount of infiltration of precipitation to groundwater. There are very few locations in Wisconsin where there is an adequate aquitard to limit infiltration and few landfills in this study are potentially in those locales. The landfills in the study that were identified as having clay surficial deposits (Table 1) were the most likely to be classified as confined aquifers. We were unable to determine trends for two of these landfills and of the remaining two landfills, one was increasing and the other was decreasing with respect to total VOCs. Additionally, we found no correlation between surficial deposits or bedrock type and any of the VOC trends we constructed. This lack of correlation was probably a result of the scale we were working in rather than there being no effect on VOC contamination from either geology or hydrogeology.

The volume of waste disposed of at each landfill didn't appear to predict whether VOC concentrations would be increasing, decreasing, or stable. However, the large landfills exhibited more trends that were either increasing or decreasing while the medium size landfills exhibited more stable trends. This suggests that larger landfills reach the stable phase of plume concentration development later than do the smaller landfills.

The remedies employed at any given landfill have shown varying degrees of success in limiting VOC concentrations downgradient from the waste mass. The only remedies that consistently resulted in a significant reduction of total VOC concentrations were groundwater and gas extraction. The success of the other types of remedies commonly employed at MSW landfills in Wisconsin was independent of any of the other site characteristics we identified in the course of this study. Where remedies were identified that had resulted in a decrease in VOC concentrations there was also a resulting impact on plume concentration development. Each time there was a significant reduction in VOC concentration caused by an engineered remedy, there was a resulting jump to a previous phase of plume development.

### *What considerations need to be made to assess whether natural attenuation is a valid remedial approach?*

Significant amounts of data need to be collected prior to making any determination about the efficacy of natural attenuation at a particular landfill. From a regulatory point of view, it is important to be able to predict the concentrations at which a plume will reach equilibrium or demonstrate that a plume has already reached equilibrium. This study was done with approximately 7-10 years of data for each landfill and yet it is believed that the VOC plumes at many landfills in this study have not yet reached a steady state with respect to concentrations. Of those sites that we believe have reached equilibrium with respect to concentration, none have approached zero. Along with a good record of VOC data, inorganic data that demonstrates the occurrence of various degradation processes should also be collected. Care should be taken to ensure that these data be collected from the same monitoring points and on the same frequencies as the VOC data.

The three-dimensional spatial distribution of monitoring points is essential for performing any analysis of VOC or inorganic data. VOC contamination at MSW landfills in Wisconsin is usually characterized by both aromatic and chlorinated solvent plumes so it is important not to neglect the third dimension. In this study, the highest levels of the BTEX compounds were present in the water table wells near the waste mass and the bulk of the chlorinated solvent compounds were present at the deeper piezometers downgradient from the waste mass. In essence, a dual monitoring network needs to be designed that accommodates the nature of both types of contaminant migration. In addition to defining the plume



spatially, there must be sentinel wells located outside the plume boundaries to ensure that the plume is not expanding.

Identifying possible receptors is of utmost importance when choosing natural attenuation as a remedial alternative because no reliable predictive tool exists that can anticipate plume extent at stabilization with regards to either contaminant mass or spatial dimensions. Consideration must be made for both the receptors at the time of implementation and any possible receptors that may come about in the future.

Gathering evidence demonstrating that natural attenuation is occurring at a rate sufficient to limit potential health risks only satisfies the question of feasibility. Any remedy that has its major component being natural attenuation must always be accompanied by an ongoing monitoring regime that is sufficient to demonstrate the continual effectiveness of natural attenuation in restricting plume growth and ultimately remediating groundwater contamination.

The current monitoring programs required by WDNR do not include analytes that provide confirmation that reductive dechlorination is proceeding to its end-point. Specifically, if vinyl chloride is degraded the end-products should be ethene, ethane, methane, and carbon dioxide. In general, these four analytes are not part of routine monitoring programs at landfills.

The data examined as part of this study suggest that reductive dechlorination is an important degradation pathway as evidenced by the finding of *cis* 1,2 dichloroethene in significant concentrations at many of the landfills. An apparent stagnation of the reductive dechlorination process results in a build-up of this compound in the groundwater. This leads one to question whether the build up is the result of absence of proper bacteria to carry out the process, lack of nutrients, lack of a suitable substrate, or a change in the oxygen content of the groundwater.

## ***Conclusions***

Old, closed, municipal solid waste (MSW) landfills represent a significant human health risk because of the large, complex spatial dimensions of their contaminant plumes, the large contaminant mass that can leach to groundwater for decades or centuries, the health effects of the substances released to groundwater, and the potential for residential development nearby. This study focused on the concentrations of total VOCs, BTEX, and chlorinated aliphatics in groundwater at MSW landfills and their concentration trends over time. Note that the data summary techniques we used in this study limit our conclusions to broad trends and do not have relevance on a site-specific basis. Therefore the trends discussed are overall site trends and do not reflect spatial differences in concentrations.

Although there were 32 sites in this study, we were unable to determine contaminant trends at every site because of variability in the data. For those sites with clear, definable contaminant trends, we found that concentrations of total VOCs have been decreasing or have stabilized at 20 of 23 sites, and at the three remaining sites, concentrations have been increasing.

Likewise, at 24 of 26 sites chlorinated aliphatic trends have been decreasing or have stabilized, and only two sites have increasing concentrations.

BTEX concentrations decreased or stabilized at 15 of 17 sites, and increased at the remaining two.

These findings are very encouraging, however, a decreasing or stable trend doesn't necessarily mean that the concentrations are significantly low or even that the plume is decreasing in size. The high number of stable and decreasing trends we found do indicate that some or all of the natural attenuation processes are occurring, assuming the sites in this study are continuous sources of VOCs to groundwater.

The three natural attenuation processes we investigated include dilution, aerobic degradation, and anaerobic degradation. Dilution appears to be the most influential abiotic process that affects VOCs as evidenced by similarities between trends of total VOCs and the trends of various inorganic parameters. The significant amount of correlation between trends using the summation of concentrations at all wells and the trends for individual wells at a site also points to dilution as the primary influence. Aerobic degradation is most important when considering the BTEX compounds, cis 1,2 DCE, and vinyl chloride. The rapid decline and the low concentrations of the BTEX compounds observed in this study indicate that aerobic degradation is occurring. Cis 1,2 DCE is primarily a degradation by-product and the high levels we observed indicate that anaerobic degradation of PCE and TCE had occurred at most sites. In addition, the disproportionately high levels of cis 1,2 DCE, at some sites, indicate that after a plume has depleted its oxygen supply it tends to remain anaerobic. While an anaerobic pathway for the degradation of cis 1,2 DCE exists, it relies upon a specific bacteria that is not widespread in the environment. Consequently, a stagnation of the degradation process occurs and concentrations of cis 1,2 DCE increase. In summary, it appears that factors influencing biodegradation and infiltration rates are most important when considering only concentration trends. Other factors may be more important when considering the spatial aspects of contaminant migration.

The VOC concentration trends we found in this study are similar to the behavior described in the literature for small-scale sites, such as underground storage tank (UST) sites and spills. At these two types of sites the BTEX compounds degrade more readily than other types of VOCs, the concentration trends follow a similar progression of phases, and the levels of cis 1,2 DCE remain high or even increase as the levels of other chlorinated aliphatics are declining. However, it appears that in contaminant plumes at MSW landfills, VOC concentrations take a much longer time to stabilize than in plumes at smaller sites. An additional difference is that VOC plumes at MSW facilities nearly always contain both BTEX

and chlorinated aliphatic constituents in addition to other non-VOC constituents, unlike contaminant plumes from UST and most spill sites.

During our preliminary review of sites that employed contamination remedies, such as landfill gas extraction, leachate collection and extraction, and various cap designs, we found that remedial actions other than landfill gas extraction produced limited effects on the various VOC trends.

### ***Further Considerations***

The inherent complexity of MSW landfills makes it difficult to predict the levels or the length of time at which a VOC plume will stabilize. Thus, an adequate monitoring regime is essential for any landfill considering natural attenuation as a remedial alternative. Prior to considering natural attenuation as a remedial measure, an extensive groundwater monitoring system must be installed to define the degree and extent of the contaminant plume in three dimensions and to monitor changes over time.

Active remedies should be considered if there is current or potential encroachment, such as water supply wells, close to a landfill. Groundwater contaminant levels at MSW landfills should be monitored throughout the remedial period to determine whether VOC concentrations will stabilize at levels below groundwater standards.

Further study into natural attenuation at MSW landfills should focus on sites with well defined contaminant plumes, including sufficient numbers of monitoring wells to characterize transition zones within the plumes both horizontally and vertically. Possible follow-up studies include a survey of plume dimensions at MSW landfills in Wisconsin; a comparison of effectiveness between passive and active remedies on controlling VOC contamination in groundwater; expansion of the routine analyte list to include methane, ethane, ethene, and carbon dioxide to determine if complete degradation is occurring and that substrate is not being consumed to produce methane; and examination of the nutrients, substrate, and bacteria present at landfills where reductive dechlorination is taking place to determine what causes the apparent stagnation at cis 1,2 DCE. In addition, a need exists to reevaluate the variance procedures for private wells using a larger sample population at landfills with known VOC contamination.

## References

- Albrechtsen, H.-J., 1994. Bacterial degradation under iron-reducing conditions. *In* Hincsee, R.E. et al. (eds.): *Hydrocarbon Bioremediation*. Lewis Publishers, Boca Raton, pp. 418-423.
- Albrechtsen, H.-J., Lyngkilde, J., Grøn, C., & Christensen, T.H., 1994. Landfill leachate-polluted groundwater evaluated as substrate for microbial degradation under different redox conditions. *In* Hincsee, R.E. et al. (eds.): *Applied biotechnology for site remediation*. Lewis Publishers, Boca Raton, pp. 371-378.
- Albrechtsen, H.-J., Smith, P.M., Nielsen, P., & Christensen, T.H., 1997. Importance of sediment fines in laboratory studies on the degradation of organic chemicals in aquifers. *Water Research*, vol. 31, pp. 2287-2299.
- Albrechtsen, H.-J., Bjerg, P.L., Ludvigsen, L., Rügge, K. & Christensen, T.H., 1999. 1. An anaerobic field injection experiment in a landfill leachate plume (Grindsted, Denmark), 2. Deduction of anaerobic (methanogenic, sulfate- and Fe(III)-reducing) redox conditions. *Water Resources Research*, vol. 35, pp. 1247-1256.
- Albrechtsen, H.-J., Smith, P.M., Nielsen, P., & Christensen, T.H., 1999. Microbial degradation potentials for organic chemicals in different size-fractions of aerobic aquifer sediment. Submitted to *Water Research*.
- Bjerg, P.L., Rügge, K., Cortsen, J., Nielsen, P.H. & Christensen, T.H., 1999. Degradation of aromatic and chlorinated aliphatic hydrocarbons in the anaerobic part of the Grindsted Landfill leachate plume: In situ microcosm and laboratory batch experiments. *Ground Water*, vol. 37, pp. 113-121.
- Christensen, T.H., Albrechtsen, H.-J., Bjerg, P.L., Rügge, K., & Kromann, A., 1996. Degradation of organic chemicals in landfills and their attenuation zones. Paper for the 7th ISWA International Congress, Yokohama, October 27 - November 1. 8 p.
- Christensen, T.H., Kjeldsen, P., Albrechtsen, H.-J., Heron, G., Nielsen, P.H., Bjerg, P.L., Hom, P.E., 1994. Attenuation of landfill leachate pollutants in aquifers. *Critical Reviews in Environmental Science and Technology*, vol. 24, no. 2, pp. 119-202.
- Eganhouse, Robert P., et al., 2001. Natural Attenuation of Volatile Organic Compounds (VOCs) in the Leachate Plume of a Municipal Landfill: Using Alkylbenzenes as Process Probes. *Ground Water*, vol. 39, no. 2, pp. 192-202.
- Fisher, Sarah R., and Kenneth W. Potter, 1989. Methods for Determining Compliance with Groundwater Quality Regulations at Waste Disposal Facilities. *Report to the Wisconsin Department of Natural Resources from the University of Wisconsin at Madison, Department of Civil and Environmental Engineering*.
- Kjeldsen, P. & Christensen, T.H., 1997. Evaluating the distribution and fate of organic chemicals in a landfill by use of a simple model. *In* Christensen, T. H., Cossu, R., & Stegmann, R. (eds.): *Sardinia '97, Sixth International Landfill Symposium, Proceedings, Volume I*. CISA. Cagliari, Italy, pp. 195-206.
- Kjeldsen, P. & Christensen, T.H., 1999. A simple model for the distribution and fate of organic chemicals in a landfill: MOCLA. Submitted to *Journal of Environmental Engineering*.
- Kromann, A., Ludvigsen, L., & Christensen, T.H., 1995. Degradability of chlorinated organic compounds in landfills. *In* Christensen, T.H., Cossu, R., & Stegmann, R. (eds.): *Sardina '95, Fifth International Landfill Symposium, Proceedings, Volume I*. CISA. Cagliari, Italy, pp. 135-142.

- Kromann, A. & Christensen, T.H., 1998. Degradability of organic chemicals in a landfill environment studied by in situ and laboratory leachate reactors. *Waste Management and Research*, vol. 16, pp. 437-445.
- Kromann, A., Ludvigsen, L., Albrechtsen, H.J., Christensen, T.H., Ejlertsson, J., & Svensson, B.H., 1998. Degradability of chlorinated aliphatic compounds in methanogenic leachates sampled at eight landfills. *Waste Management and Research*, vol. 16, no.1, pp. 54-62.
- Ludvigsen, L., Albrechtsen, H.J., Heron, G., Bjerg, P.L. & Christensen, T.H., 1998. Anaerobic microbial redox processes in a landfill leachate contaminated aquifer (Grindsted, Denmark). *Journal of Contaminant Hydrology*, vol. 33, pp. 273-291.
- Ludvigsen, L., Albrechtsen, H.J., Ringelberg, D., Ekelund, F., & Christensen, T.H., 1999. Distribution and composition of microbial populations in a landfill leachate contaminated aquifer (Grindsted, Denmark). *Microbial Ecology*, vol. 37, no. 3, pp. 197-207.
- Lyngkilde, J. & Christensen, T.H., 1992. Fate of organic contaminants in the redox zones of a landfill leachate pollution plume (Vejen, Denmark). *Journal of Contaminant Hydrology*, vol. 10, pp. 291-307.
- Mace, Robert E., et al., 1997. Extent, Mass, and Duration of Hydrocarbon Plumes from Leaking Petroleum Storage Tank Sites in Texas. *Geological Circular 97-1, Bureau of Economic Geology, The University of Texas at Austin, Austin, Texas.*
- McNab, Walt W. Jr., et al., 1999. Historical Case Analysis of Chlorinated Volatile Organic Compound Plumes. Lawrence Livermore National Laboratory publication number UCRL-AR-133361, Livermore, California.
- Nielsen, P.H., Bjarnadottir, H., Winter, P.L., & Christensen, T.H., 1995. In situ and laboratory studies on the fate of specific organic compounds in an anaerobic landfill leachate plume. II: Fate of aromatic and chlorinated aliphatic compounds. *Journal of Contaminant Hydrology*, vol. 20, pp. 51-66.
- Nielsen, P.H., Bjerg, P.L., Nielsen, P., Smith, P., & Christensen, T.H., 1996. In situ and laboratory determined first-order degradation rate constants of specific organic compounds in an aerobic aquifer. *Environmental Science & Technology*, vol. 30, pp. 31-37.
- Rügge, K., Bjerg, P.L., & Christensen, T.H., 1995. Distribution of organic compounds from municipal solid waste in the groundwater downgradient of a landfill (Grindsted, Denmark). *Environmental Science & Technology*, vol. 29, pp. 1395-1400.
- Rügge, K., Bjerg, P.L. & Christensen, T.H., 1998. Natural attenuation of aromatic and chlorinated aliphatic compounds: Comparison of field and laboratory experiments. In *Groundwater Quality: Remediation and Protection*. Proceedings of the GQ '98 Conference, Tübingen, Germany, 21-25 September. IAHS Press, Wallingford, Oxfordshire, pp. 205-211.
- Rügge, K., Bjerg, P.L., Pedersen, J.K., Mosbæk, H. & Christensen, T.H., 1999. An anaerobic field injection experiment in a landfill leachate plume (Grindsted, Denmark), 1. Experimental set-up, tracer movement and fate of aromatic and chlorinated compounds. *Water Resources Research*, vol. 35, pp. 1231-1246.
- Sims, Judith L., Joseph M. Suflita, and Hugh H. Russell, 1991. Reductive Dehalogenation of Organic Contaminants in Soils and Ground Water. *EPA Ground Water Issue, EPA/540/4-90/054.*
- Wiedemeier, Todd H., Hanadi S. Rifai, Charles J. Newell, and John T. Wilson. *Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface*. New York, NY: John Wiley & Sons, Inc., 1999.

Table 1. List of Landfills, Overall Trends, and Geology

License Number	Landfill Name	Total VOC Trend	Chlorinated Aliphatics Trend	Overall BTEX Trend	Surficial Geology	Bedrock Geology	Depth to Bedrock
85	Chippewa Falls City LF	Decreasing	Decreasing	Decreasing	Sand & Gravel	Sandstone	50-100 ft
108	Rice Lake City LF	Decreasing	Decreasing	Decreasing	Sand & Gravel	Sandstone	>100 ft
1953	Refuse Hideaway LF	Decreasing	Decreasing	Decreasing	Sand	Carbonates	5-50 ft
2637	La Crosse County LF	Decreasing	Decreasing	Decreasing	Loam	Sandstone	< 5 ft
2892	Marathon County LF	Decreasing	Decreasing	Decreasing	Sand	Igneous/Metamorphic	50-100 ft
35	Boscobel City LF	Decreasing	Decreasing	Undetermined	Loam	Carbonates	5-50 ft
162	Baraboo City LF	Decreasing	Decreasing	Undetermined	Sand	Sandstone	>100 ft
942	Village of Argyle	Decreasing	Decreasing	Undetermined	Loam	Carbonates	< 5 ft
2342	Shawano City LF	Decreasing	Decreasing	Undetermined	Clay	Sandstone	>100 ft
2680	Dane County LF#1	Decreasing	Decreasing	Undetermined	Sand & Gravel	Sandstone	50-100 ft
1935	Madison City-Sycamore LF	Increasing	Increasing	Increasing	Sand	Sandstone	5-50 ft
107	Metropolitan Refuse District Inc	Increasing	Increasing	Stable	Sand & Gravel	Sandstone	50-100 ft
1890	WMWI-Green Lake Sanitary LF	Increasing	Stable	Increasing	Clay	Sandstone	50-100 ft
314	Clintonville City LF	Stable	Decreasing	Decreasing	Loam	Igneous/Metamorphic	>100 ft
3306	Dane County Truax	Stable	Decreasing	Decreasing	Sand	Sandstone	>100 ft
738	St. Croix River Valley LF	Stable	Decreasing	Undetermined	Sand	Igneous/Metamorphic	50-100 ft
893	Watertown City LF	Stable	Stable	Decreasing	Sand	Carbonates	5-50 ft
1356	WMWI-Reclamation	Stable	Stable	Decreasing	Sand & Gravel	Carbonates	50-100 ft
1768	Osseo Area Sanitary LF	Stable	Stable	Decreasing	Sand & Gravel	Sandstone	50-100 ft
943	Jongetjes LF	Stable	Stable	Stable	Sand	Carbonates	>100 ft
1858	Arcadia City LF	Stable	Stable	Stable	Loam	Sandstone	< 5 ft
1972	Junker Sanitary LF	Stable	Stable	Stable	Sand	Sandstone	50-100 ft
2246	Waupun City LF	Stable	Stable	Stable	Sand	Carbonates	5-50 ft
126	Durand City	Undetermined	Undetermined	Undetermined	Loam	Sandstone	>100 ft
287	Black River Falls City LF	Undetermined	Decreasing	Undetermined	Sand & Gravel	Sandstone	5-50 ft
611	Winnebago County LF	Undetermined	Decreasing	Undetermined	Clay	Carbonates	50-100 ft
2565	Juneau County LF	Undetermined	Stable	Undetermined	Sand	Sandstone	< 5 ft
7	Majerus LF	Undetermined	Undetermined	Undetermined	Sand	Carbonates	50-100 ft
843	Town of Shelby LF	Undetermined	Undetermined	Undetermined	Loam	Sandstone	< 5 ft
912	Merrill City LF	Undetermined	Undetermined	Undetermined	Sand	Igneous/Metamorphic	>100 ft
3108	WMWI-Parkview	Undetermined	Undetermined	Undetermined	Clay	Carbonates	>100 ft

Note: The overall trends for landfills with multiple groups of wells were determined by considering the locations and amounts of data contributed by each group of wells at each landfill. For instance, if one group of wells had 10 years worth of data and another had only 3 years then the first group was thought to more representative of the overall trend.

Table 2. Size Classifications, Remedies, and Overall VOC Trends

License Number	Size Class	Total VOC Trend	Chlorinated Aliphatics Trend	BTEX Trend	Gas Extraction System	Leachate Collection	Leachate Extraction	Clay Liner
00108	Large	Decreasing	Decreasing	Decreasing				
01953	Large	Decreasing	Decreasing	Decreasing	Y		Y	
02637	Large	Decreasing	Decreasing	Decreasing	Y		Y	Y
02892	Large	Decreasing	Decreasing	Decreasing	Y	Y		Y
02680	Large	Decreasing	Decreasing	Undetermined			Y	
01935	Large	Increasing	Increasing	Increasing	Y	Y		Y
00107	Large	Increasing	Increasing	Stable				
03306	Large	Stable	Decreasing	Decreasing	Y			
01356	Large	Stable	Stable	Decreasing	Y	Y		
01972	Large	Stable	Stable	Stable	Y	Y		
00611	Large	Undetermined	Decreasing	Undetermined	Y	Y		Y
00007	Large	Undetermined	Undetermined	Undetermined	Y			
03108	Large	Undetermined	Undetermined	Undetermined		Y		Y
00085	Medium	Decreasing	Decreasing	Decreasing		Y		
00035	Medium	Decreasing	Decreasing	Undetermined				
00162	Medium	Decreasing	Decreasing	Undetermined				
00942	Medium	Decreasing	Decreasing	Undetermined				
02342	Medium	Decreasing	Decreasing	Undetermined				
01890	Medium	Increasing	Stable	Increasing	Y			
00314	Medium	Stable	Decreasing	Decreasing				
00738	Medium	Stable	Decreasing	Undetermined		Y		Y
00893	Medium	Stable	Stable	Decreasing	Y			
01768	Medium	Stable	Stable	Decreasing				
00943	Medium	Stable	Stable	Stable				
01858	Medium	Stable	Stable	Stable				
02246	Medium	Stable	Stable	Stable				
00126	Medium	Undetermined	Undetermined	Undetermined				
00287	Medium	Undetermined	Decreasing	Undetermined				
02565	Medium	Undetermined	Stable	Undetermined	Y	Y		Y
00843	Medium	Undetermined	Undetermined	Undetermined				
00912	Medium	Undetermined	Undetermined	Undetermined	Y			

Figure 1. Example of Total VOC and Inorganic trends tracking at WMWI-Green Lake Sanitary LF

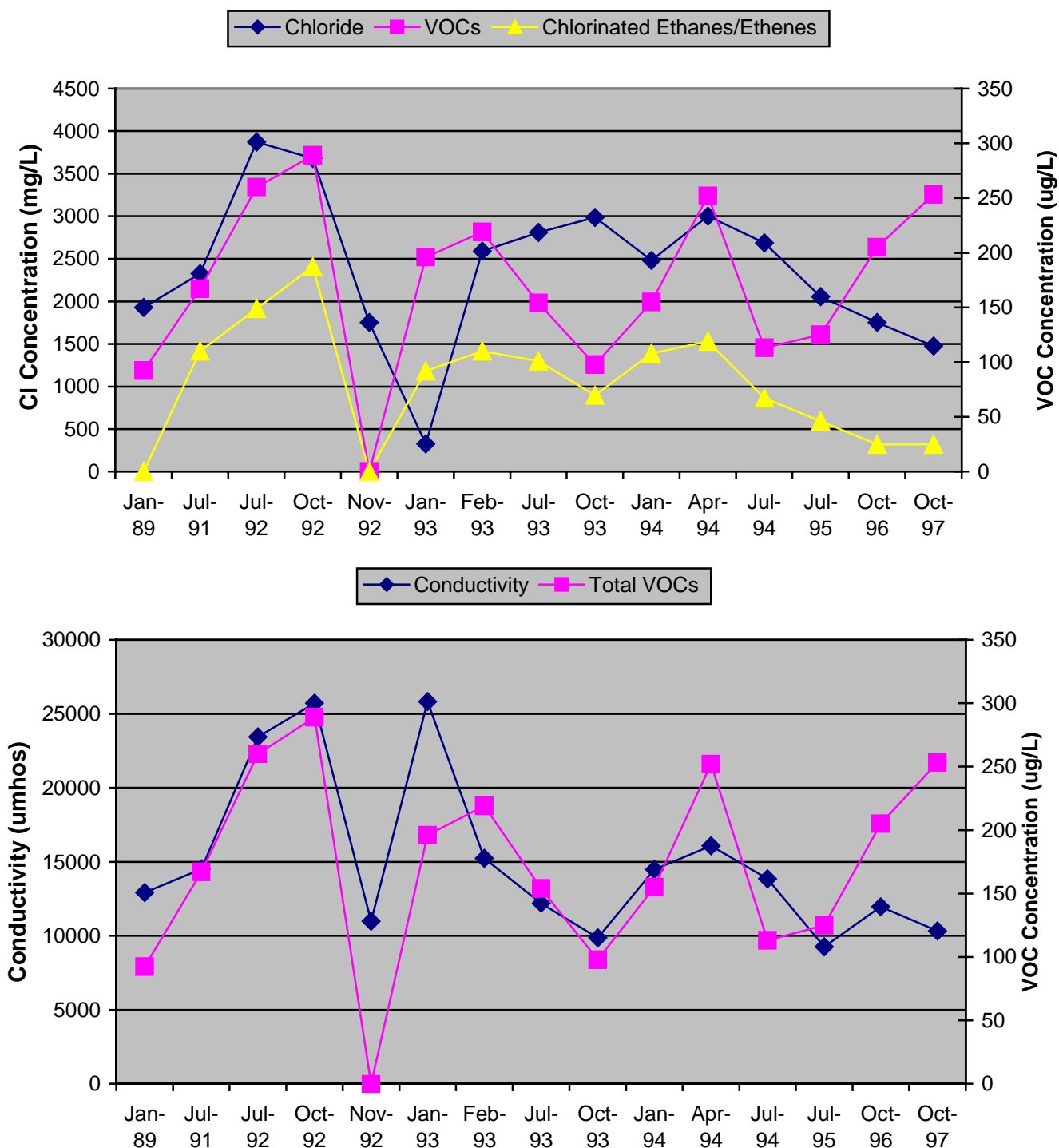




Figure 2. Example of “Good” Visual Correlation between Total VOCs in All Wells and in Individual Wells at Junker Landfill (License #1972)

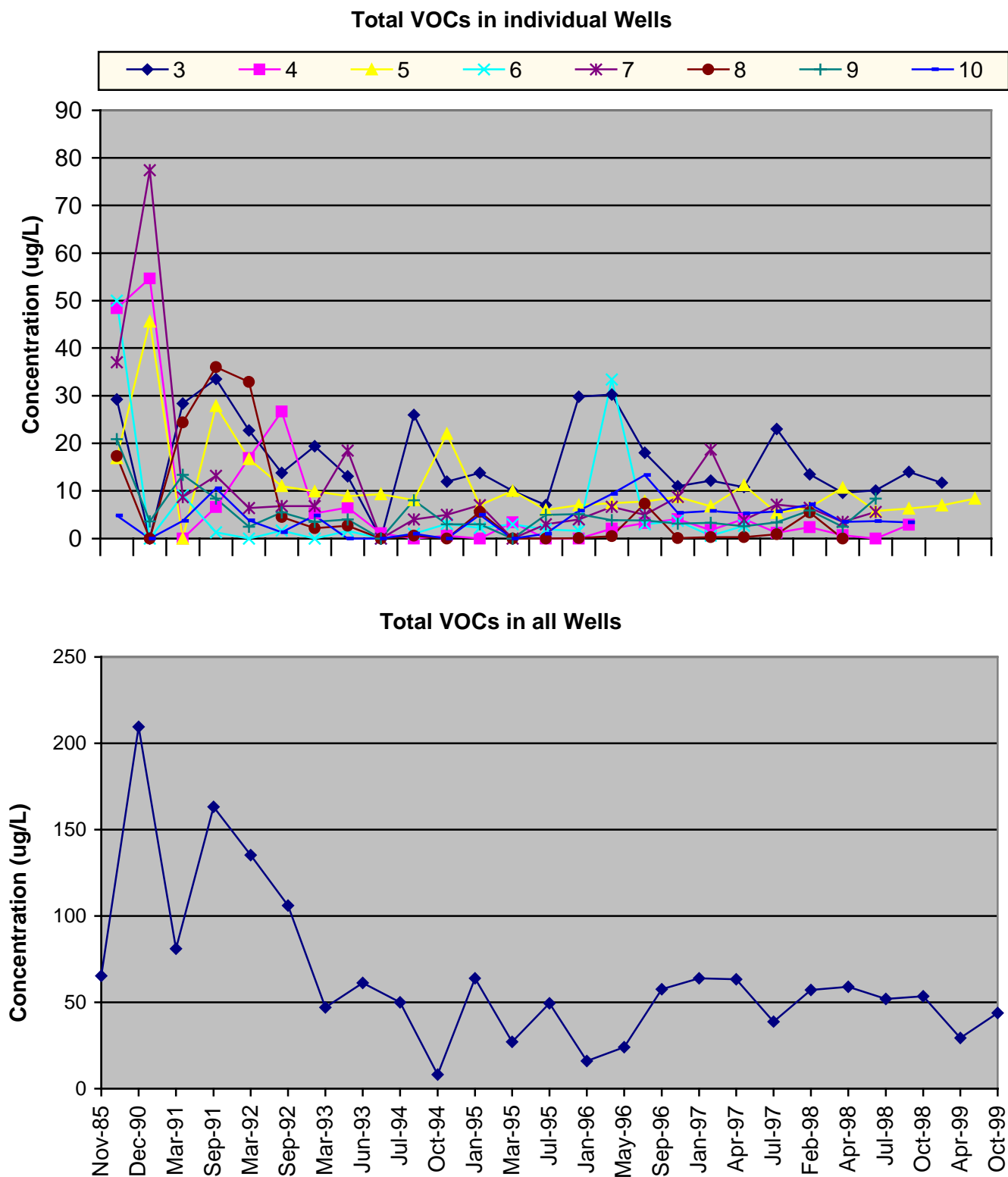


Figure 3. Chlorinated Ethene Concentrations through time at Metropolitan Refuse District Landfill

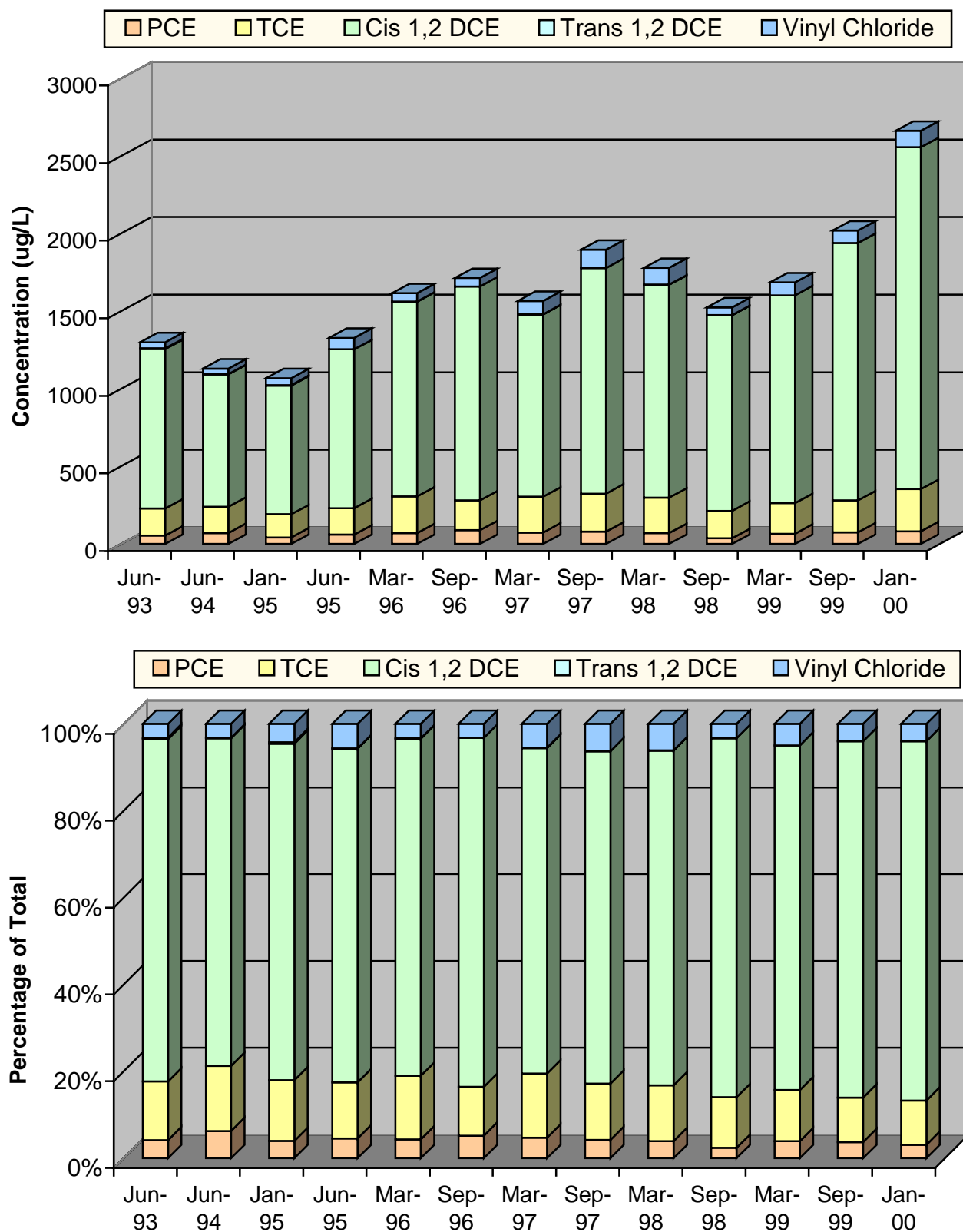


Figure 4. Chlorinated Ethene Concentrations through time at Rice Lake Landfill

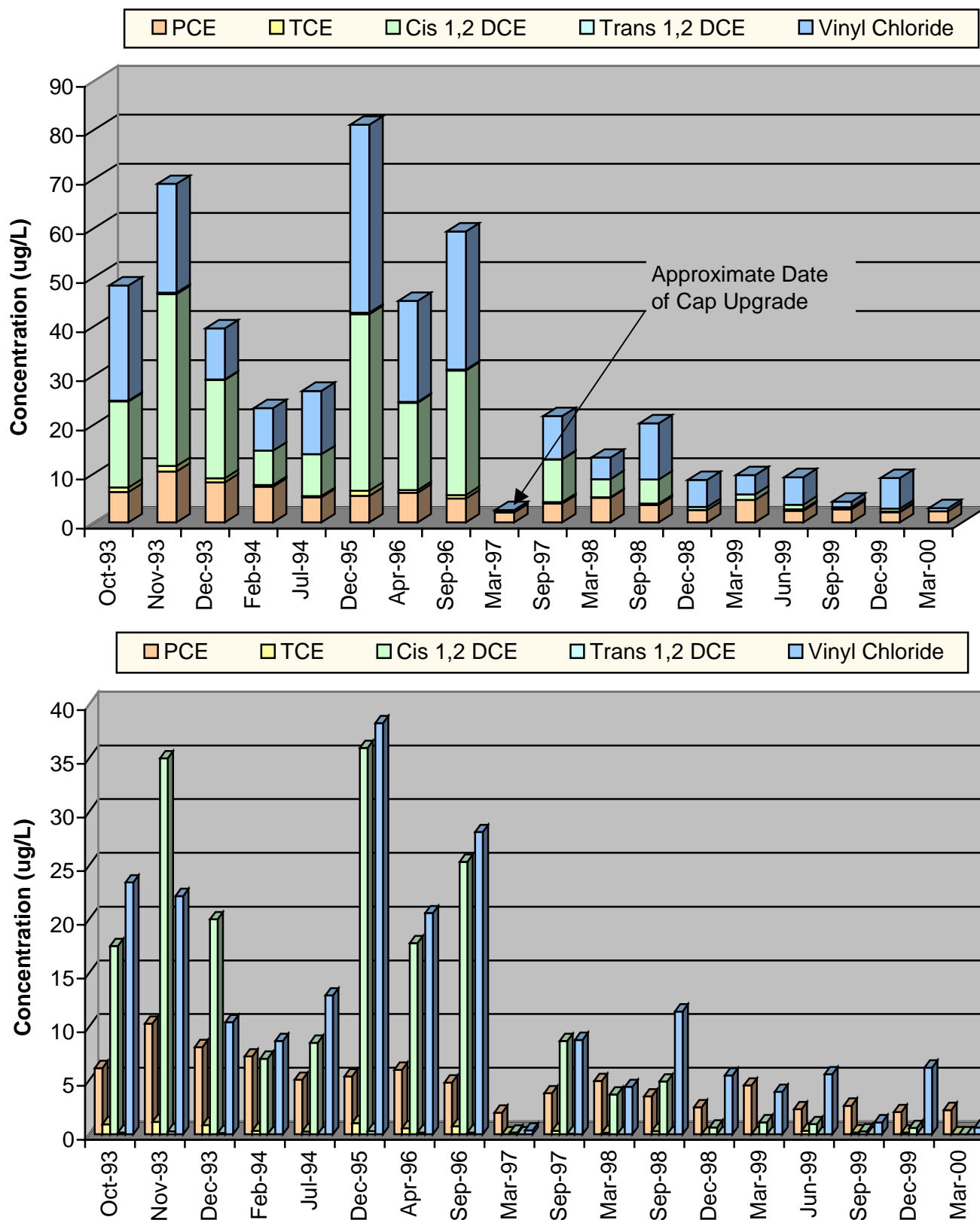


Figure 5. Chlorinated Ethene Concentrations through time at the City of Waupun Landfill

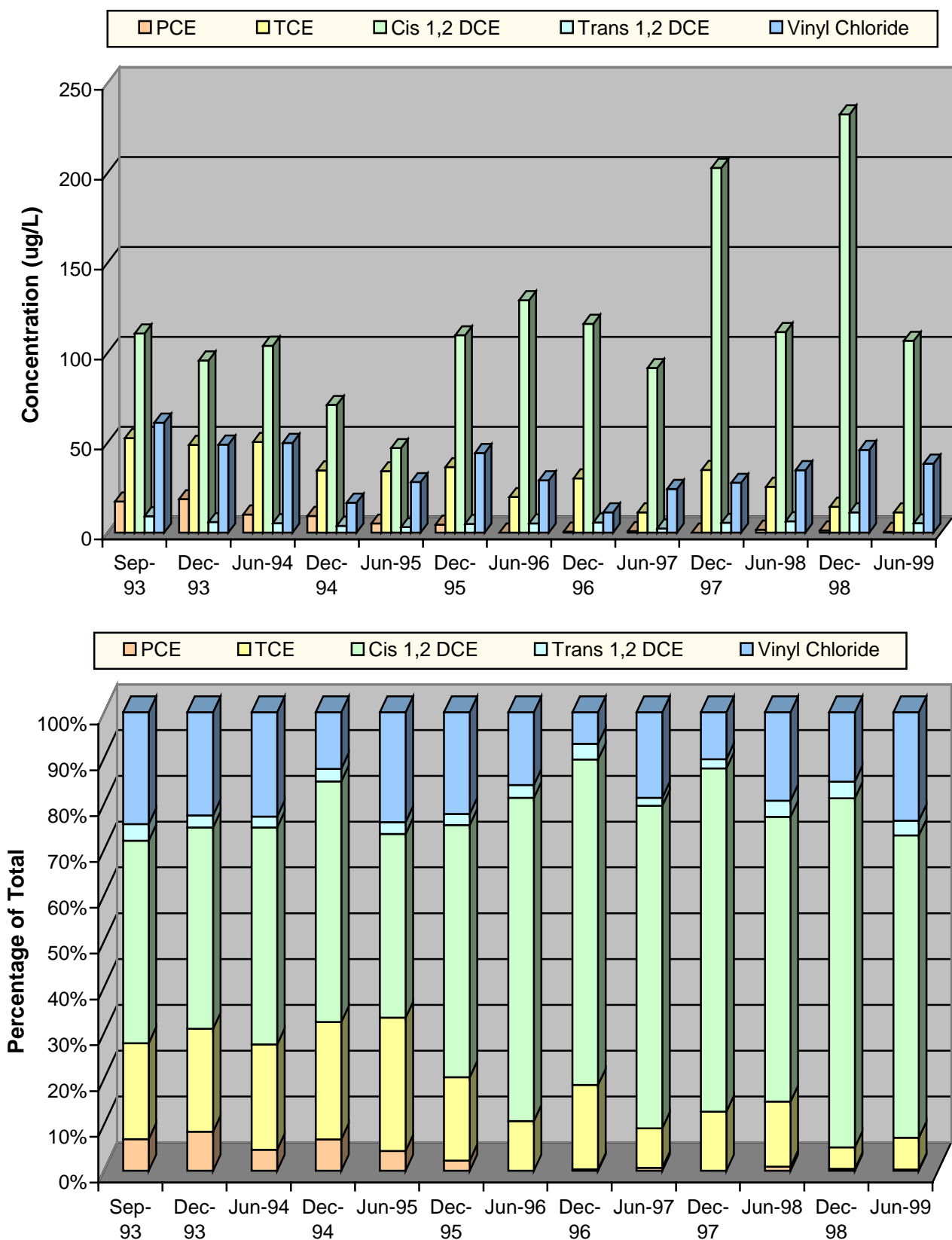


Figure 6. Chlorinated Ethene Concentrations through time at City of Durand Landfill

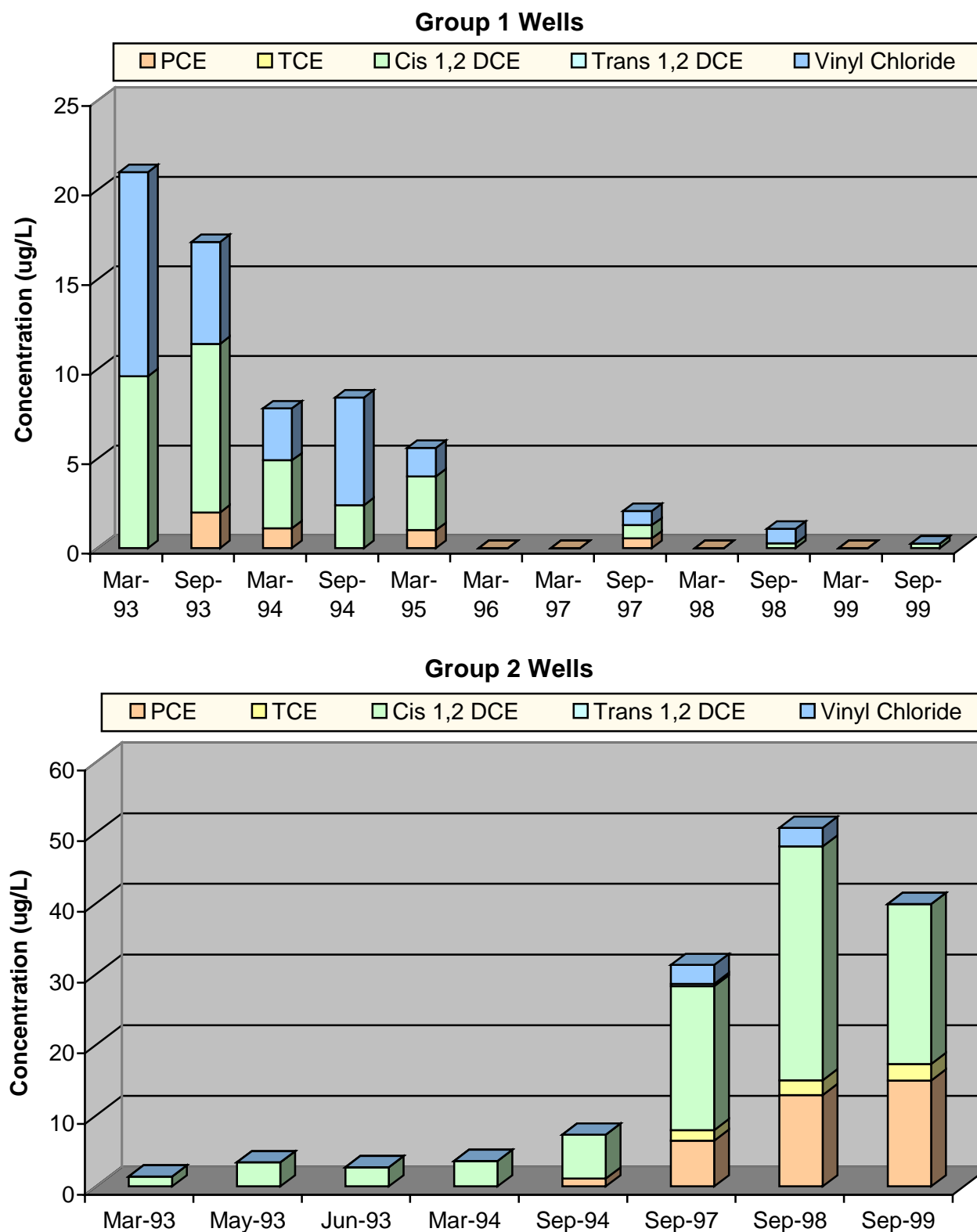


Figure 7. Chlorinated Ethene Concentrations through time at City of Boscobel Landfill

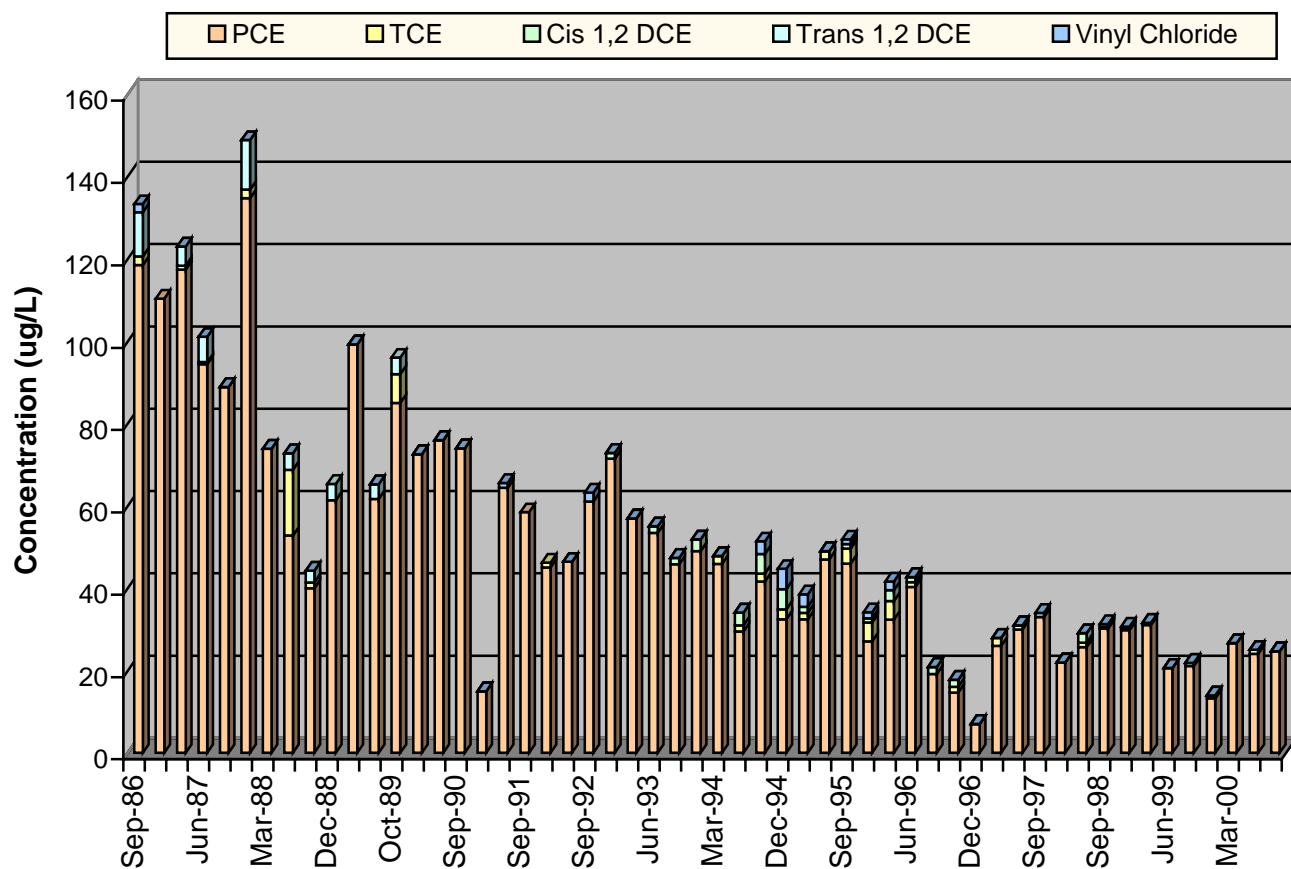
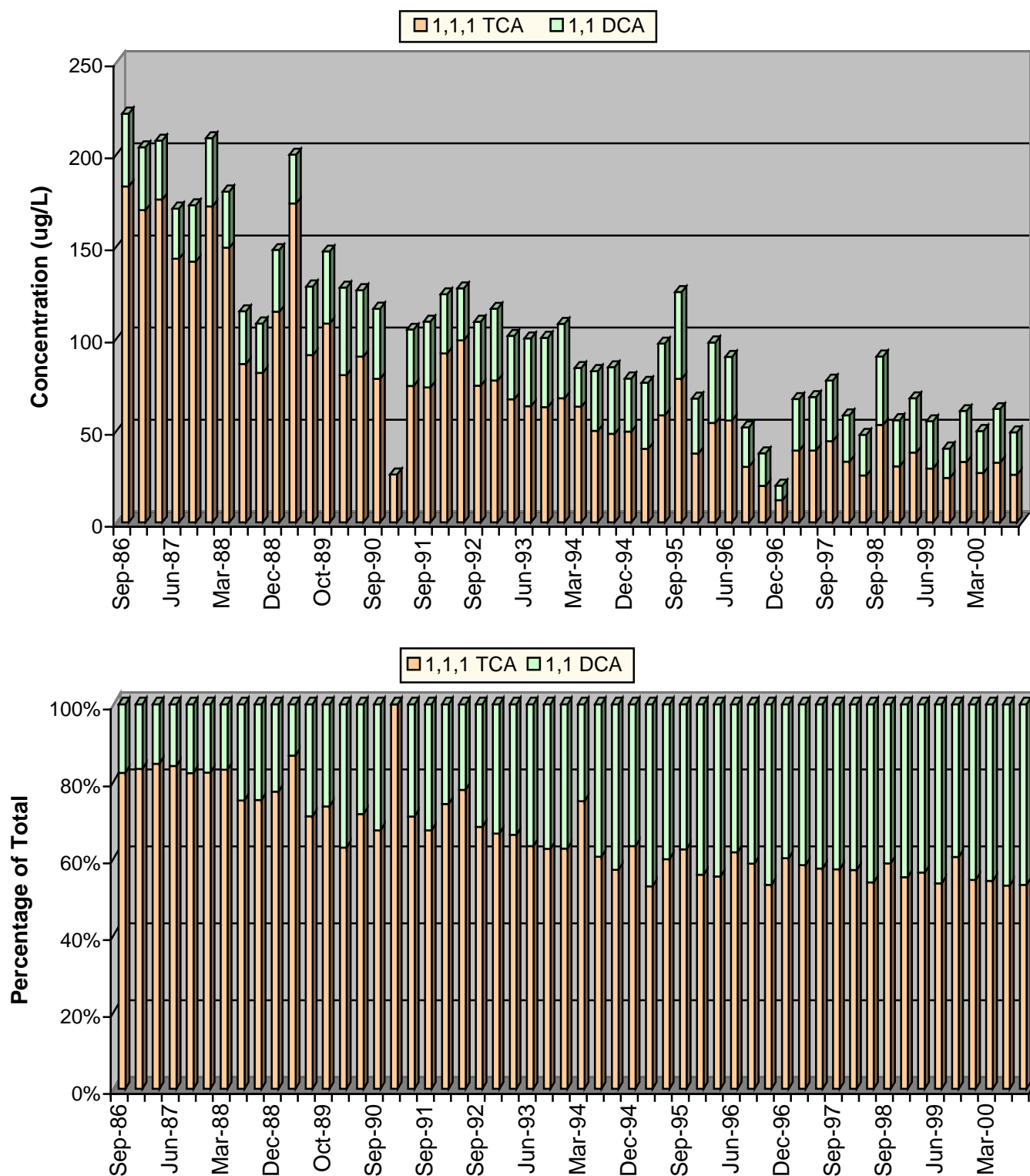


Figure 8. Chlorinated Ethane Concentrations through time at City of Boscobel Landfill



## Location of Study Sites

